Water-Soluble Photopolymers for Rapid Prototyping of Cellular Materials

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Received 9 August 2003; accepted 4 January 2005
DOI 10.1002/app.22025

ABSTRACT: Commercial light-sensitive resins for Rapid Prototyping of cellular materials are often unsuitable for different molding techniques because removal of the mold uses thermal decomposition at temperatures of up to 600°C. In this study, a resin formulation based on water-soluble polymers was developed and evaluated regarding its usability as sacrificial mold material. The base monomer dimethylacrylamide gave fast curing and excellent polymer solubility. Methacrylic acid was found to be a useful comonomer to improve mechanical strength and feature resolution. The latter criterion was also improved by adding poly(vinyl pyrrolidone) as filler and by using a hydrolytically cleavable crosslinking agent such as methacrylic acid anhydride. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 2286–2298, 2005

Key words: water-soluble polymers; lithography; photopolymerization; molding; radical polymerization

INTRODUCTION

State of the art: rapid prototyping (rp) of cellular materials

Most cellular materials for engineering applications (e.g., polymeric foams for packaging applications, aluminum foams, ceramic foams for biomedical applications) are made by adding a foaming agent. During polymerization of the liquid monomer, the foaming agent expands into mostly spherical gas bubbles, which define the porosity of the foam after complete solidification. By this approach, the internal geometry of the obtained cellular solid can only be controlled within certain statistical limits.

If the envisaged application requires exact control size and shape of the pores, alternative approaches must be used. For the fabrication of metallic lightweight structures, sandwich panels[1] filled with truss-like cellular designs were developed. These structures are usually made by welding or laminating individual layers and stacking them up to obtain the final structure. Because the geometry of cellular solids typically exhibits many overhanging features, conventional fabrication techniques that allow the precise control over the final geometry (e.g., CNC machining) are no viable option for the fabrication of such structures.

RP techniques offer a much more versatile approach to print arbitrary shapes starting from a computer aided design (CAD) file. Furthermore, the task of process planning for the fabrication of cellular solids by RP involves significantly less effort than traditional methods. Several commercially available RP techniques have already been used for the fabrication of cellular solids. Suitable methods are Selective Laser Sintering (SLS),[2] Stereolithography (SLA),[2,3] Fused Deposition Modeling (FDM),[4] and the Solidscape Modelmaker[5] (Table I). Issues that have to be taken into account are the achievable feature resolution and whether the desired shape can be built without support structures, which have to be removed mechanically. SLS and FDM offer advantages regarding the removal of support structures. The unsintered, loose powder in the SLS machine can easily be removed even in the case of complex cellular materials with open porosity. FDM offers wash-away support materials, which can be dissolved in water. SLA uses mechanically removable supports, but offers significant advantages regarding achievable feature resolution.

RP has already been used, mostly in combination with ceramic forming techniques, to fabricate scaffolds for tissue engineering applications.[5–8] First, experiments with sacrificial RP molds[3] have shown that composite materials can be molded, but that further investigations are necessary to improve the feature resolution of the final RP part and to decrease the time necessary for the fabrication. With wax-based processes especially (e.g., Solidscape Modelmaker), the

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Contract grant sponsor: Hochschuljubiläumsstiftung of the City of Vienna.
Contract grant sponsor: Austrian Science Foundation FWF; contract grant number: P15859.

Journal of Applied Polymer Science, Vol. 97, 2286–2298 (2005)

TABLE I
Comparison of Various RP Processes

System	Resolution *xy* (mm)	Minimal layer thickness *z* (mm)	Build volume *xyz* (mm × mm × mm)	Vertical build speed (mm/h)	Build duration for test part (h)
Envisiontec Perfactory	0.05–0.07	0.03	70 × 60 × 50	15–20	4
Solidscape Modelmaker	0.08	0.01–0.08	300 × 150 × 230	0.5–2.5	400
3D-Systems SLS	—	0.1	370 × 320 × 445	8	2.5
FDM	0.2	0.25	600 × 500 × 600	—	—

build duration for more complex structures can reach impractical values.

Issues which need to be considered when RP parts are used as sacrificial molds include the following points:

- It must be possible to remove the sacrificial mold without damaging the final part. Removal can be achieved mechanically (if the part contains no undercuts), thermally, by melting, or by dissolution of the mold in an appropriate solvent.
- There should be no chemical interaction between the mold and the part material during solidification of the final part. Certain mold materials can inhibit the polymerization of the part material at the interface between mold and unpolymerized liquid. Silicone materials especially are known to inhibit, for instance, the polymerization of monomers used in ceramic gel-casting.
- If delicate parts with fragile features have to be molded, a weak and soft mold material (e.g., wax) is usually more suitable than stiffer and stronger materials (e.g., heavily crosslinked polymers). When the mold is removed, it might swell (due to the influence of the solvent) or expand (thermal expansion). This change in geometry can introduce cracks into the final part if the mold material is significantly stronger than the part material.
- Conventional SLA materials can only be removed by thermal decomposition. Thermally unstable part materials (e.g., ceramic–polymeric composites) can therefore not be molded with this process. Thermally stable materials (e.g., ceramics) can in principle be molded, but because of the thermal mismatch between part- and mold-material complex geometries might get distorted or damaged during the debinding process. An example for this problem is depicted in Figure 1.
- RP processes that can deposit thermoplastic or soluble materials (e.g., FDM or Solidscape Modelmaker) have a significantly lower feature resolution than SLA, which makes it difficult to shape cellular solids suitable for biomedical applications.

The use of soluble photocurable polymers could be an ideal process with respect to feature resolution and build speed. In the literature,[9,10] numerous monomers, such as acrylic acid, methacrylic acid, methacrylamide, *N*,*N*-dimethylacrylamide, vinyl pyrrolidone, etc., are described to give water-soluble polymers by radical polymerization. Such monomers were proposed to find application in thickeners for oil recovery,[11] as biodegradable detergents,[12] and for controlled drug release.[13] Other monomers[14] of interest are acryl-

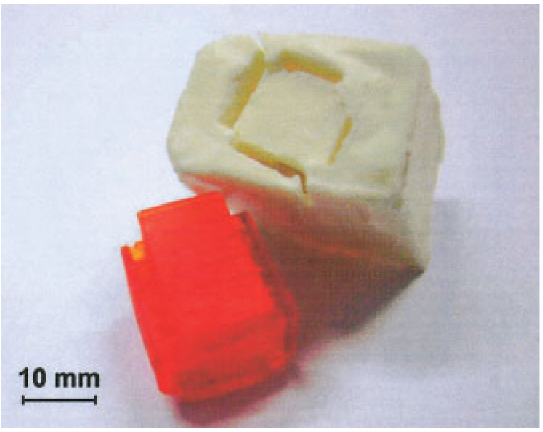


Figure 1 Ceramic part made by gel-casting into SLA mold. The cracks in the ceramic part originate from the thermal mismatch between mold material and part material.

RP materials

As shown, RP is a suitable method for fabricating parts with high shape complexity and good feature resolution. Problems arise, when more advanced materials than metals, polymers, or ceramics are required. For biomedical applications especially, there is a need for new materials, which can be shaped by RP (e.g., composite materials).

The route proposed in this work uses sacrificial water-soluble molds made by stereolithography. Traditionally, either nonsoluble RP parts made by stereolithography or thermoplastic parts made by SLS or deposition processes are used as molds for shaping cellular structures based on biomaterials. Compared to these conventional routes, the use of water-soluble photocurable resins offers a number of advantages:

amide, 2-acrylamido-2-methylpropan-1-sulfonic acid, sodium vinyl sulfonate, or sodium-4-vinylbenzenesulfonate. Because the latter are solid monomers, polymerization in aqueous solutions or in other liquid monomers, which lead to copolymers, has to be considered. Recently, a plotter process was claimed, where part material (e.g., polystyrene) and sacrificial support material for undercut features (e.g., dimethylacrylamide) were simultaneously applied.[15] To the best knowledge of the authors, until now the use of water-soluble polymers for stereolithography has not been described.

EXPERIMENTAL

Irgacure 819 (I819) and Irgacure 784 (I784) were received as a gift from Ciba SC (Basel, Switzerland) and all other photoinitiators and monomers were purchased from Aldrich (Munich, Germany). All compounds were used without further purification. Diisopropylamide was prepared according to the literature.[16]

Test rods (60 × 10 × 2.5 mm) were prepared from monomer mixtures by using 3 wt % photoinitiator and a silicone mold. Irradiation was carried out for up to 30 min by using a medium-pressure mercury lamp (Hereaus TQ-150) that was positioned 24 cm above the sample. After 30 min, the distance was reduced to 13 cm for monomers with low reactivity.

Shore hardness D of the test rods was examined following DIN 53505 by using a Hildebrand Durometer HD 3000. For simple and reproducible determination of the polymer solubility, a defined part of the test rod (10 × 10 × 2.5 mm) was used. This sample was magnetically stirred with 250 rpm at room temperature in 20 mL of distilled water in a covered Erlenmeyer flask. The time for entire dissolution was determined. Experiments were also carried out at 50°C and under alkaline (0.1*N* and 1*N* NaOH) or acidic (0.1*N* and 1*N* HCl) conditions.

The UV absorption was measured with a Hitachi U-2001 spectrometer with spectrophotometric-grade acetonitrile as solvent.

Photo-DSC was conducted with a modified Shimadzu DSC 50 equipped with a homemade aluminum cylinder.[17] Filtered UV light (400–500 nm) was applied by a light guide (Efos-Novacure) attached to the top of the aluminum cylinder. The light intensity at the tip of the light guide (500 mW/cm^2) was measured by an internal radiometer. The measurements were carried out in an isothermal mode at room temperature under air with 0.5 or 3 wt % PI. The mass of the samples was 10 ± 0.2 mg. The time to reach the maximum polymerization heat (t_{max}), the double bond conversion (DBC), and the rate of polymerization (R_p) were determined. A theoretical heat of polymerization for the calculation of the DBC and R_P was assumed for acrylates and acrylamides to be H_0 = 80.5 kJ/mol, for acrylic acid, H_0 = 77.5 kJ/mol, for methacrylates, H_0 = 57.5 kJ/mol, and for *N*-vinyl pyrrolidone, H_0 = 54.7 kJ/mol.[18] Additionally, the influence of the initiator concentration was investigated.

RESULTS AND DISCUSSION

Evaluation of various photocurable formulations

The key step in this new route to biomimetic cellular materials is the development of photocurable resins leading to water-soluble polymers. The following various requirements have to be met:

- The monomers should be commercially available, offer a high rate of polymerization, and have a suitable viscosity.
- The photoinitiator (PI) has to be soluble in the formulation and the absorption characteristics should match the emission characteristics of the digital light projection (DLP) lamp (usually in the visible range). Additionally, high reactivity of the PI is one of the key factors.
- Finally, the polymer obtained by this process should have low shrinkage during polymerization, adequate hardness and stiffness even at elevated temperature, smooth surfaces, and good solubility in water or acidic/alkaline media.

Screening of suitable photoinitiators

PIs are the key component in light curable formulations. By irradiation with UV or visible light, reactive species such as radicals, cations, or anions are formed that are capable of initiating the polymerization of suitable monomers. Because DLP is based on visible light, PIs absorbing above 400 nm are needed. Therefore, bisacylphosphine oxide I819 and titanocene I784 were chosen as cleavable Type I PIs, which are known to have outstanding reactivity.[19] Further suitable initiators that have found widespread application are based on camphorquinone (CQ) and 2-isopropylthioxanthone (ITX). Because these compounds belong to the Type II PIs, suitable coinitiators were selected [dimethylamino benzoic acid ethylester (DMABE) and triethanolamine (TEA)]. The chemical structures are depicted in Figure 2. All these PIs show the photobleaching effect (i.e., the chromophore of the PI is destroyed under irradiation and therefore deeper layers can be polymerized by the incident light).

To get an overview about the absorption characteristics of the selected PIs, UV–Vis spectra were measured in the range of 10^{-2} to 10^{-6} mol/L in acetonitrile (Fig. 3). The molar extinction coefficient (ε_{max}) and the wavelength of maximum absorption (λ_{max}) of all initiators are summarized in Table II.

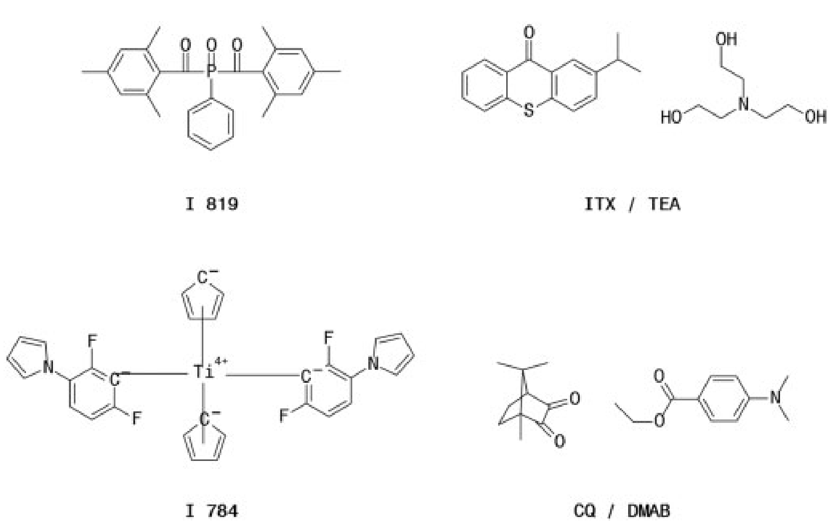


Figure 2 Photoinitiators.

I819 and ITX gave absorption up to 450 nm and for CQ a maximum of the n--π^* transition centered at 469 nm was found. I784 showed the strongest absorption in the visible range. It is well known that a high extinction coefficient is desired, but this does not necessarily lead to high photoreactivity.[19] Therefore, it was of interest to investigate the photoreactivity of these PIs in a model monomer.

Photo-DSC experiments were carried out, allowing a fast and accurate evaluation of various important parameters with one single measurement. The time to reach the maximum polymerization heat ($t_{\max}$) reveals the activity of the formulation. Furthermore, the area below the trace (ΔH_p) corresponds to DBC [eq. (1)

$$\mathrm{DBC} = \frac{\Delta H_P \times M}{\Delta H_{0,P}} \tag{1}$$

where ΔH_P is the heat of polymerization (J/g); M is the molecular weight of the monomer (g/mol); and $\Delta H_{0,P}$ is the theoretical heat of polymerization of the monomer (J/mol).

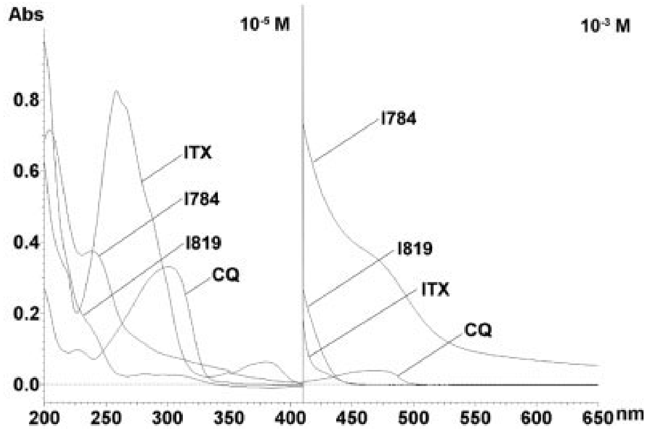


Figure 3 UV–Vis spectra of the PIs.

Initial rates of polymerization (R_p) were calculated from the height h (J/g) of the maximum of the plots following

$$R_P = \frac{h\rho}{\Delta H_{0,P}} \tag{2}$$

where R_P is the rate of polymerization (mol l^{-1} s^{-1}); h is the peak height (mW/mg); and ρ is the density of the monomer (g/L).

Comparison of all initiators was carried out by using filtered UV light (400–500 nm) and 0.5 wt % PI in N,N-dimethyl acrylamide (DMA). An equimolar amount of coinitiator was used in the case of the Type II PIs. A layer thickness of ~50 μm was chosen to obtain results comparable to the DLP machine. Figure 4 shows the graphs of these photoexperiments. It was found that bisacylphosphine oxide I819 is especially suitable due to the high absorption in the 400- to 500-nm range, the outstanding reactivity of the formed radicals and sufficient solubility in the resin formulation. $t_{\max}$, the most important parameter for

TABLE II
UV–Vis Absorption of the PIs

PI	$\lambda_{\max}$ [nm]	$\varepsilon_{\max}$ [L cm^{-1} mol^{-1}]
ITX	259	82400
	383	9520
CQ	301	33000
	469	40
I 819	282	3300
	366	520
I 784	239	37500

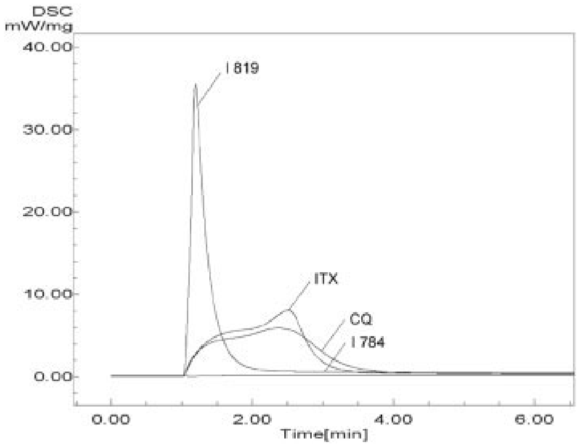


Figure 4 Photo-DSC of DMA with different PIs.

the building time of the object, was on the order of 8 s for I819 compared to more than 80 s for all other initiators. Also, the R_p was more than five times higher. Only DBC was somewhat lower (65%) compared to ITX and CQ (72%).

To optimize the latter parameter, the influence of the PI concentration of I819 on the curing behavior was investigated. It was found that DBC could be enhanced to >70% by using >3 wt % of PI (Fig. 5).

By reduction of exposure time, construction time can be significantly reduced if sufficient double bonds are converted to maintain mechanical properties. By using photo-DSC experiments in combination with a shutter technique, different exposure times were simulated (Fig. 6). The data revealed that, within an irradiation time of only 5 s, a DBC of >70% was obtained at a layer thickness of 50 μm.

Additionally, the influence of oxygen inhibition was determined in this formulation. It was found that under nitrogen atmosphere R_p and DBC were only marginally higher. Only $t_{\max}$ could be improved by 25%. Nevertheless, all further studies were carried out under aerobic conditions, because inert atmosphere can hardly be achieved in this RP unit.

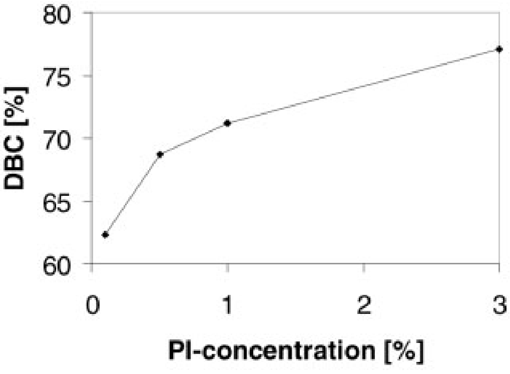


Figure 5 DBC versus PI concentration using 3 wt % I819.

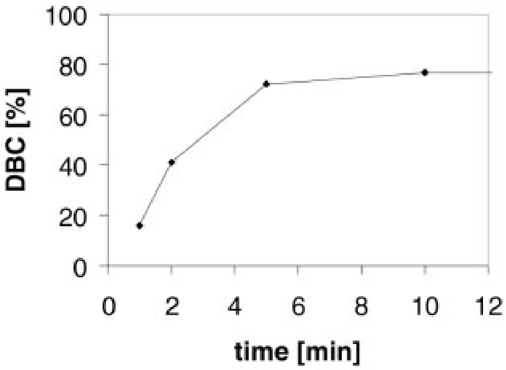


Figure 6 DBC versus irradiation time using 3 wt % I819.

To confirm that I819 is the most suitable PI, a set of photo-DSC experiments was carried out with vinyl pyrrolidone (VP) as monomer. As expected, compared to DMA, a significantly lower photoreactivity was found, but I819 gave outstanding reactivity in comparison with I784, ITX, and CQ. DBC was found to be >80% versus <12% for all other initiators.

Screening of monomers

Water-soluble polymers as sacrificial structures are easily accessible by photopolymerization of a wide range of commercially available monomers. Reactivity of the monomers was determined by using photo-DSC experiments with 3 wt % I819 as PI (Fig. 7). Data are summarized in Table III. Aqueous solutions of solid monomers were not tested by this method because evaporation of the water during irradiation leads to inaccurate results. As expected, the group of acrylate-based monomers gave the highest photoactivity. Therein, DMA and acrylic acid (AA) performed best

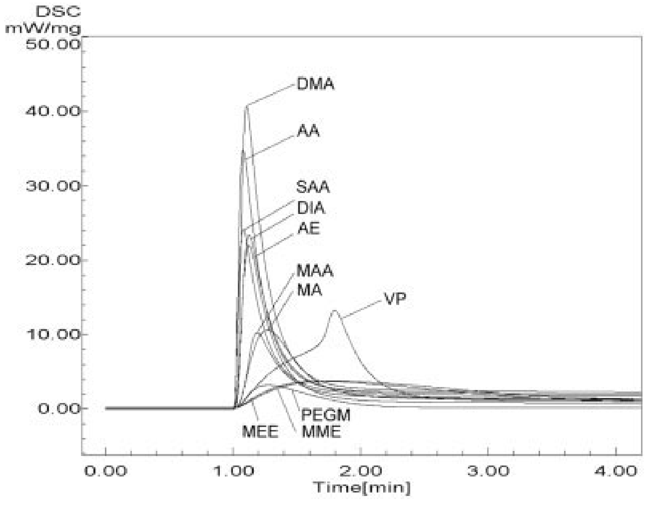
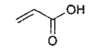
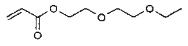
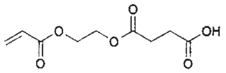
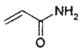
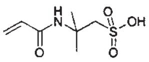
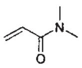
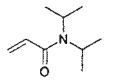
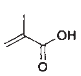
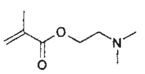
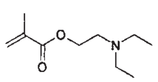
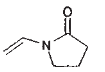
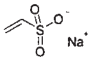
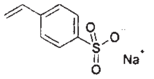


Figure 7 Photo-DSC of monomers (for abbreviations see Table III).

TABLE III
Properties of Monomers and Polymers Thereof

Monomer	Abbreviation	Structure	PC[a]	Photo-DSC			Solubility [min]			Shore D
				t_{max} (s)	DBC (%)	R_P (mol $L^{-1}s^{-1}$)	H_2O	0.1*N* HCl	0.1*N* NaOH	
Acrylic acid	AA		L	4.8	43	0.444	[b]	[b]	[b]	71
Acrylic acid 2-(2-ethoxy-ethoxy)-ethyl ester	AE		L	7.2	90	0.264	[b]	[b]	[b]	[c]
Succinic acid mono-(2-acryloyloxy-ethyl)ester	SAA		L	4.8	91	0.347	1440	[d]	300	10
Acrylamide	AAm		S (62%)	[e]	[e]	[e]	[b]	[d]	[d]	63
2-Acryloylamino-2-methyl-propane-1-sulfonic acid	AMPS		S (54%)	[e]	[e]	[e]	[b]	[d]	[b]	38
N,N-Dimethyl-acrylamide	DMA		L	6.6	77	0.464	90	120	[d]	69
N,N-Diisopropyl-acrylamide	DIA		L	7.8	50	0.208	[b]	[d]	[d]	[f]
Methacrylic acid	MA		L	16.2	36	0.147	1440	[d]	60	89
2-Methyl-acrylic acid 2-dimethylamino-methyl ester	MME		L	41.4	68	0.045	[b]	30	[d]	25
2-Methyl-acrylic acid 2-dimethylamino-ethyl ester	MEE		L	46.2	71	0.041	[b]	60	[d]	28
N-Vinyl-pyrrolidin-2-one	VP		L	47.4	82	0.231	150	[b]	[d]	73
Sodium, vinylsulfonate	VSS		S (30%)	[e]	[e]	[e]	30	[d]	30	[f]
Sodium; 4-vinyl-benzenesulfonate	SVS		S (22%)	[e]	[e]	[e]	30	[d]	30	[f]

[a] Physical condition: L, liquid; S, solid; photopolymerization of an aqueous solution (X wt %).
[b] Insoluble, only swelling occurs.
[c] Too flexible.
[d] No improvement expected.
[e] Not determined.
[f] Too brittle.

because of their low molecular weight and thus high mobility. Low DBC of the latter monomer might be explained by the precipitation of the polymer during irradiation. Similar tendencies but decreased reactivity were observed for methacrylate-based monomers. In addition, different types of vinyl-based monomers (but-3-enoic acid, undec-10-enoic acid, 4-vinyl-pyridine, *N*-vinyl-imidazole, and VP) were investigated, but only VP gave sufficient photoactivity.

Properties of the polymers

As already mentioned, apart from the photopolymerization activity of the monomer, mechanical properties and solubility of the polymer also have to be considered. Test specimens (60 × 10 × 2.5 mm) were prepared by irradiation of the formulation in a suitable silicone mold. For this set, only 0.5 wt % I819 was chosen as PI to ensure entire curing also in deeper layers. Mechanical properties were characterized by measurement of Shore Hardness D. Solubility, one of the important properties, was determined by stirring a defined specimen in aqueous solutions and determination of the time for entire dissolution. It has to be noted that, for good reproducibility, stirring conditions must be kept constant. Monomers containing amine functionalities were also tested under acidic conditions, because salt formation should improve the

TABLE IV
Solubility (min) of Homopolymers at RT and 50°C

	H_2O		0.1N HCl		0.1N NaOH	
Polymer from	RT	50°C	RT	50°C	RT	50°C
SAA	[a]		[b]		300	60
DMA	90	60	[b]		[b]	
MA	1440	300	[b]		60	45
MME	[a]		30	15	[b]	
MEE	[a]		60	30	[b]	
VP	150	90	[a]		[b]	

[a] Insoluble.
[b] Not determined because no improvement expected.

solubility significantly. For the same reason, monomers with carboxylic acid or sulfonic acid residues were tested under alkaline conditions. To investigate the characteristics of solid monomers, diluted and saturated aqueous solutions were irradiated. In addition, aqueous solutions of methacrylic amide (19 wt %) and maleic acid (43 wt %) and *N*-hydroxymethyl acrylamide (60 wt %) were irradiated. The latter one formed only a rubberlike polymer, which was not suitable for further investigations, and the former ones gave no polymer. AA, DIA, VSS, and SVS gave very brittle and inhomogeneous polymers. This might be explained by the insolubility of the polymer in the monomer solution. Therefore, these monomers are not suitable, although the latter two showed excellent water solubility. AE, SAA, MME, and MEE are also unsuitable as base monomer due to the poor mechanical properties of the polymers, caused by the long and flexible side chain. Under neutral conditions, only poly-DMA and poly-VP showed sufficiently fast dissolution and good mechanical properties. Poly-MA showed good overall performance but needed alkaline conditions for fast dissolution. Excellent hardness of this polymer could be ascribed to intermolecular hydrogen bonds.

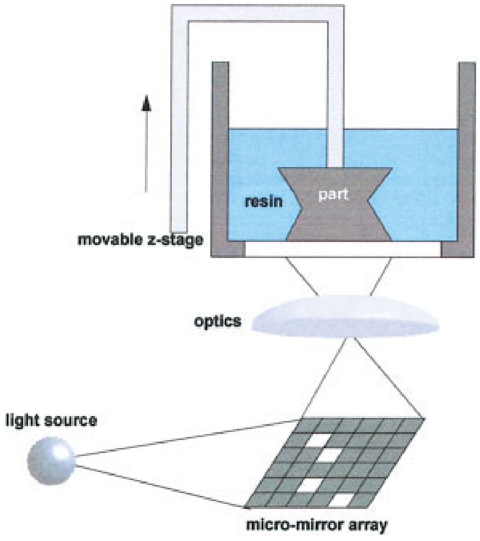


Figure 8 Digital light projection: working principle of the utilized machine.

To accelerate dissolution, a set of experiments at elevated temperature (50°C) was carried out (Table IV). It was found that, in the case of polymers insoluble at room temperature, elevated temperatures gave no improvement. For RT-soluble polymers, the dissolution time could be decreased by a factor of up to 4.

Additional experiments were carried out polymerizing VP and DMA in the presence of water (0–50%) to improve the solubility by preswelling of the polymers. Besides decreased mechanical properties, improved solubility was only obtained for VP with more than 5 wt % water content.

Rapid prototyping

Rapid prototyping was carried out by using a SLA unit from Envisiontec (Figs. 8 and 9). The machine is based on a digital mirror device (DMD), which is used to project a bitmap onto a light-sensitive resin. The bitmap is generated from a sliced CAD file. The projected bitmap is white in those regions where polymerization should take place; all other areas are kept black. The bitmap is projected onto the resin through a silicone-coated vat. The exposed regions of the resin

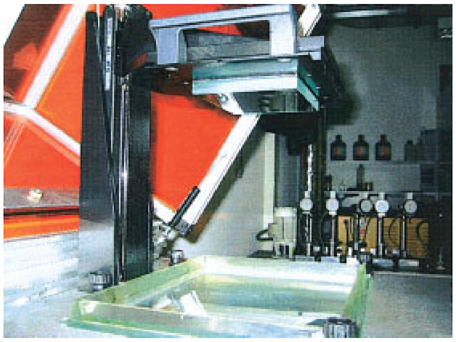


Figure 9 Resin tank and movable glass plate.

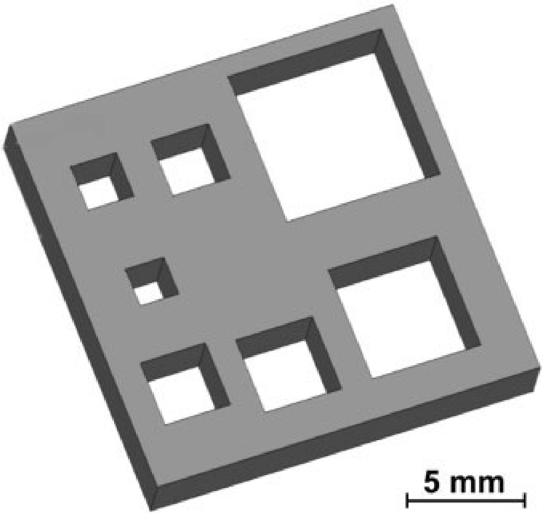


Figure 10 2D model.

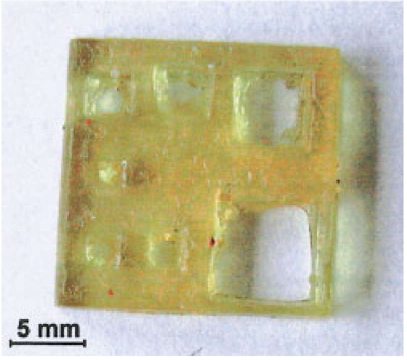


Figure 11 Test part obtained from water-soluble photocurable material (DMA).

solidify between the silicone and a movable glass plate. This glass plate is elevated after light exposure, and the solidified resin detaches from the silicone base. After liquid resin has filled the gap between the first-part layer and the silicone, the next irradiation step can be started. By this approach, the final part is built up layer by layer. The thickness of the individual layers is controlled mechanically by moving the glass plate by using a stepper motor. This method allows a precise control of the layer thickness. Furthermore, the layer thickness can be kept small compared to coating methods used in conventional stereolithography.

For the first set of experiments, a 2D-model was designed (Fig. 10) to keep the building time short. The *xy* resolution which can be achieved with the different monomers was evaluated and several instrument parameters such as light intensity, irradiation time, and layer thickness were varied. DMA, MA, and VP were chosen as suitable monomers because of the sufficient solubility and good mechanical properties of the polymer found in the preceding studies.

Despite the variation of light intensity, irradiation time, and layer thickness, no polymer was formed with MA and VP, probably because of their relatively low photoreactivity. Only poor results were obtained with DMA concerning resolution and mechanical properties (Fig. 11). This might be attributed to the solubility of the polymer in the monomer. Dissolution experiments in DMA proved the poly-DMA is dissolved under stirring within 4 h.

Optimization of formulation

For further experiments, DMA was chosen as suitable base monomer because of the best overall performance. To tune the formulation with respect to the resolution, mechanical properties, solubility, and shrinkage, a series of experiments with different comonomers was carried out. Additionally, it was believed that fillers could have a positive influence on the overall performance (shrinkage, water solubility, resolution).

Comonomers

Further attempts to improve the solubility and mechanical properties were carried out by the addition of various comonomers. MME was tested because of the excellent solubility under weak acidic conditions, although reduced mechanical properties could be expected. Furthermore, VSS, SVS, and MA were investigated as comonomer for DMA, because pure polymers gave promising solubility and mechanical

TABLE V
Shore D and Solubility of DMA with Various Comonomers

Comonomer	wt %	Shore D	Solubility (min)		
			H_2O	0.1*N* HCl	0.1*N* NaOH
—	—	69	90	120	[a]
MME	5	68	90	90	[b]
	20	65	300	30	[b]
VSS	5	76	120	[b]	150
	20	70	90	[b]	150
SVS	5	73	120	[b]	120
	20	55	90	[b]	90
AA	5	62	150	[b]	150
	20	67	720	[b]	180
MA	5	78	120	[b]	150
	20	70	300	[b]	180
AAm	5	75	120	[b]	[b]
	20	80	150	[b]	[b]
MAm	5	76	120	[b]	[b]
	20	72	150	[b]	[b]
AMPS	5	72	120	[b]	[b]
	20	[c]	[c]	[c]	[c]

[a] Insoluble.
[b] Not examined since no improvement expected.
[c] Comonomer incompatible.

TABLE VI
Shore D and Solubility in Water of DMA with PVP as Filler

PVP (%)	M_{PVP} (g/mol)	Shore D	Solubility (min)
0		69	90
13.8	360,000	61	90
37.5	[a]	65	45
52.3	10000	68	15

[a] Unknown (10000>x>360000).

properties. VSS was received as 30% aqueous solution. Additionally AA, AAm, AMPS, and methacrylic amide (MAm) were tested as comonomers because improved mechanical properties due to intermolecular hydrogen bridging and good solubility could be expected. Because alkaline conditions should improve solubility of most of these copolymers, dissolving experiments were also carried out in 0.1*N* NaOH. The results are summarized in Table V.

Adding up to 20% to DMA increased solubility and only a marginal reduction of the mechanical properties was found. As expected, under neutral conditions, decreasing solubility was obtained with increasing content of MME. Under acidic conditions, the solubility was optimized even with 20 wt % MME.

For all other monomers, by adding a low amount (5 wt %) of comonomer to DMA, the desired effect of improved mechanical properties was obtained in most cases. Generally, higher concentrations of comonomer led to incompatibility in the monomer mixture, and thus, decreased hardness was found. AA and AAm were the only exceptions. With a low amount of comonomer AA, incompatibility in the polymer was visible. The best mechanical properties were obtained at higher contents (20%) of AAm as comonomer.

In all cases, decreased solubility in water compared to the pure monomers was found. Surprisingly, dissolution experiments under alkaline conditions did not give any improvements, although in most cases carboxylic or sulfonic acid groups are present in the comonomer. Usually, nearly identical dissolution time was obtained compared to the experiments in water.

Additionally, MME was investigated as flexibilizer with excellent solubility in combination with brittle polymers derived from AA and MA. Hardness of AA was increased by using MME as comonomer and only insoluble material was obtained. Explanation could be found by salt formation between carboxy and amino functionality, leading to a crosslinked network. The same applies to MA.

TABLE VII
Photo-DSC Data of DMA and MMA

Monomer	t_{max} (s)	DBC (%)	R_P (mol L^{-1} s^{-1})
DMA	6.6	77	0.464
MAA	11.4	27	0.161

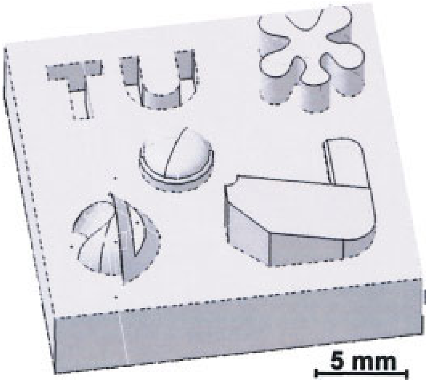


Figure 12 3D model for RP.

Due to the good overall performance obtained with MA as comonomer, the dissolving behavior of the polymer in the monomer was tested. Even under long-time stirring, the test specimen remained unchanged. Therefore, MA was chosen as suitable comonomer.

Fillers

For further improvement of water solubility, and to reduce shrinkage which leads to inexact reproduction of the part material, fillers with excellent water solubility were investigated. Additionally, increased formulation viscosity might result in better resolution, because radical diffusion is limited and dissolution behavior of the monomer for the polymer is reduced. Fillers based on renewable resources, such as sucrose, carboxy-modified starch, and polydextrose, which are known as fillers with good water solubility, were chosen and applied in a concentration range of 5 to 50% in DMA. Due to the poor solubility of the pure fillers in DMA, diluted aqueous solutions were applied. In all cases, 5, 20, and 50 wt % of sucrose solutions (17, 34, and 68 wt % in water) gave decreased hardness and

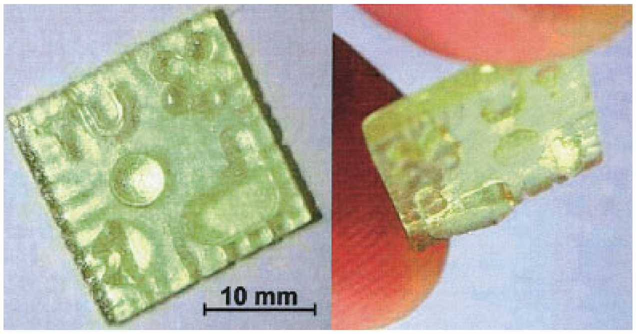


Figure 13 Poly-MSA-3D.

TABLE VIII
Solubility of DMA-MAA Copolymers

MAA (wt%)	Shore D	H_2O		0.1N NaOH		1N NaOH	
		RT	50°C	RT	50°C	RT	50°C
0	69	90 min	60 min	[a]	[a]	[a]	[a]
17	71	[b]	<1 day	<1 day	12 h	[b]	<1 day
50	74	[b]	[b]	3 day	<1 day	3 day	<1 day
83	79	[b]	[b]	[b]	<1 day	3 day	<1 day
100	80	[b]	[b]	[b]	<1 day	5 day	<1 day

[a] Not examined since no improvement expected.
[b] Insoluble.

inferior solubility. Saturated solutions of carboxymethyl starch (38 wt %) and polydextrose (61 wt %) were added to DMA in concentrations of 5, 20, and 50 wt %. Improved solubility was only achieved by adding 20 and 50 wt % of polydextrose, but cloudy and softer polymers were obtained.

Therefore, we used commercially available and, in DMA, highly soluble poly(vinyl pyrrolidone) (PVP). This seems to be a suitable method to incorporate PVP, which suffers from low-polymerization speed of the monomer. Table VI summarizes the results obtained by application of PVP with different molecular weights. The higher the molecular weight, the lower the amounts of PVP that were added to avoid a too strong increase in viscosity.

By using high amounts of low-molecular PVP gave perfect solubility in water, while maintaining the mechanical properties. Low amounts of high-molecular PVP (360,000) resulted in decreased mechanical properties and no change of solubility.

Crosslinking agent

Increasing the viscosity during polymerization (e.g., by bifunctional monomers) is a suitable pathway to reduce diffusion of the radical and dissolution of the formed polymer, which has a detrimental effect on the final geometry. Crosslinkers should also lead to an increase of mechanical strength. Because typical crosslinking agents lead to swelling and an insoluble polymer network, methacrylic anhydride (MAA) as a hydrolytically cleavable monomer was chosen. To obtain information about the suitability of this monomer for RP, reactivity was evaluated by Photo-DSC. The experiments gave good reactivity (t_{max}) for MAA, but decreased DBC and R_p compared to DMA due to network formation (Table VII). Additionally, RP experiments with 3D structures and pure MAA were carried out and gave the best results obtained so far (Figs. 12 and 13). Cracks at the border of the part were caused by the high degree of crosslinking.

To investigate the influence of this crosslinker on DMA, test specimens with different ratios DMA : MMA were prepared. Results of solubility are summarized in Table VIII. As expected, a drawback of this modification was significantly longer dissolution times. Already 17 wt % of MAA increased the dissolution time to 24 h, while slightly improved mechanical properties were obtained. As expected, the mechanical properties increased linearly with the amount of MAA in the formulation. To obtain acceptable times, elevated temperature (50°C) and alkaline conditions were investigated. At room temperature, neat poly-MAA needed dissolution times of up to 5 days in 1*N* NaOH. At 50°C, dissolution time could be reduced to less than 24 h independent of the amount of MMA.

TABLE IX
Optimization of DMA with MA, PVP (360.00 g/mol), and MAA

Mixture	DMA	MA	PVP	MAA	Hardness[a]	Resolution[b]
1	35	35	11	19	++	+
2	21	50	11	19	++	++
3	25	55	13	7	++	+
4	40	40	13	7	++	+++
5	35	35	13	17	++	++
6	36	36	9	18	+	++
7	0	71	11	18	B	+−

[a] ++ = very brittle; + = brittle; B = too brittle.
[b] +++ = very good; ++ = good; + = edges inexact; +− = small square filled.

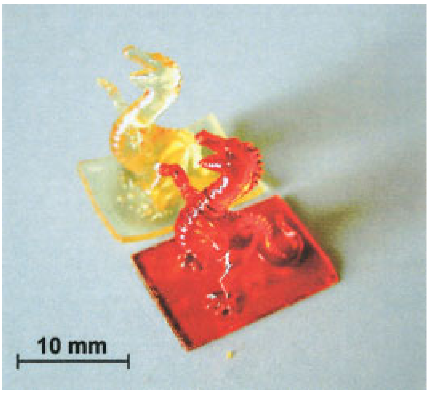


Figure 14 3D structure.

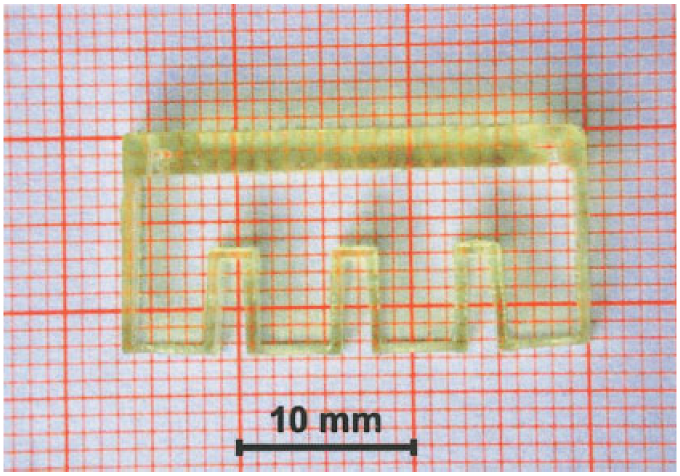


Figure 15 Cooling channel.

To further decrease the dissolution time, methanol was applied as cosolvent. Surprisingly, significantly longer dissolution times were found when 1 : 1 mixtures of methanol and 1*N* NaOH were used.

Rapid prototyping of optimized formulations

The preliminary investigations indicated that PVP is suitable as filler and that MA as comonomer leads to improved mechanical properties, but a decrease of dissolution time. Various RP experiments were carried out with the 2D model (Fig. 10) to study the effect of each component. Less satisfactory results were obtained, probably due to dissolution of the polymer by the monomer. High-molecular PVP (M = 360,000) was used for these experiments, because high amounts of low-molecular PVP (M = 10,000) suppressed polymer formation under these conditions. By using low amounts of alkaline-cleavable crosslinker MAA, improved feature size could be expected. Mixtures of DMA with MAA and PVP or MA with varying ratios gave only little improvement. The results of mixtures of all four components are summarized in Table IX. First, satisfactory parts were obtained with mixtures containing 35% DMA, 35% MA, 11% PVP, and 19% MAA (w/w). Higher contents of MA (Mixture 2) gave improved resolution but still not good general results. It was found that 7 wt % MAA (Mixture 3 and 4) are sufficient to give good hardness and resolution. Tests without DMA (Mixture 7) gave too brittle products and confirmed the necessity of the base monomer.

With Mixture 4, a series of more extensive experiments was carried out. Figure 14 shows a 3D structure (left: water-soluble polymer; right: commercially available, highly crosslinked photopolymer) and Figure 15 shows a cooling channel made by RP. Building times for these objects were on the order of 60 min. Generally, it has to be mentioned that by using this RP technique it is also possible to fabricate several objects at the same time, thus reducing the average building time significantly. The cooling channel was dissolved in alkaline solution at elevated temperatures (Fig. 16). At 50°C, entire dissolution was observed within 2.5 h.

RP experiments with cellular 3D structures gave skins on overhanging features which could be ascribed to the photobleaching effect of the initiator. To avoid penetration of incident light into deeper layers, different types of light absorbers were investigated. Dyes based on anthraquinone derivatives have similar absorption range compared to acylphosphine oxide I819. 1,4-Dihydroxyanthraquinone was applied at very low concentration because of the well-known deactivation found in UV stabilizers based on 2-hydroxbenzophenones. Dye concentrations (*c*) were cal-

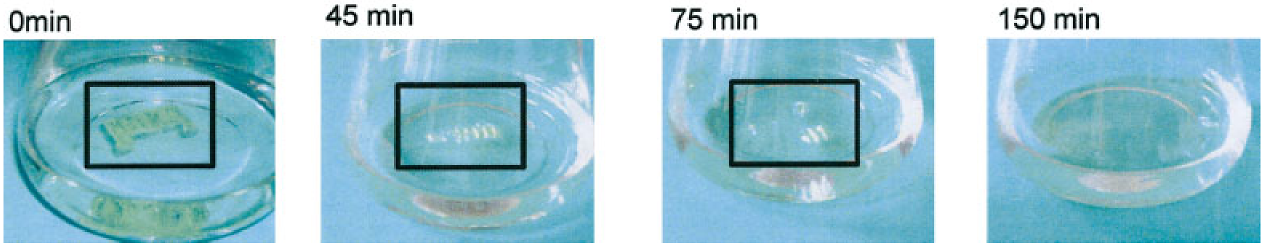


Figure 16 Dissolution of cooling channel in 1*N* NaOH at 50°C.

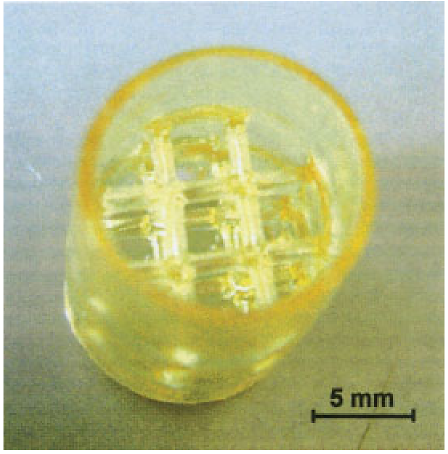


Figure 17 Cellular 3D structure.

culated according to the Lambert–Beers law ($A = d\varepsilon c$). Values for absorption (A) were tested in the order 0.001 to 0.1. The layer thickness (d) was chosen to be 30 μm, which is the usual layer height in the RP experiments. The poor results concerning resolution and polymer formation at higher concentrations led us to dyes based on 2-hydroxyanthraquinone, which do not quench that strong. 2,6-Dihydroxyanthraquinone (0.1 wt %) gave similar feature size as in experiments without any dye, but efficiently suppressed skin formation (Fig. 17).

Molding

With the optimized formulation, it was possible to fabricate soluble cellular structures (Fig. 18, left images). These structures can serve as sacrificial mold for various thermosetting polymers (e.g., silicone; Fig. 18, right image), which can only be obtained by using a soluble mold material. Thus, this route enables fabrication of parts with severe undercuts by utilizing SLA molds, and the spectrum of accessible materials can be significantly extended.

CONCLUSIONS

Results from the investigation of the test specimens and preliminary RP experiments indicated that several parameters are essential to obtain optimum curing performance and polymer properties.

Besides high reactivity, the main components of the formulation should show excellent solubility in water after polymerization. Combinations of monomers based on (carboxylic) acids and tertiary amines are unsuitable because of network formation, due to crosslinking by salt bridges.

Swelling of the polymer during and after irradiation caused by the monomer significantly influences resolution and mechanical properties. By the addition of comonomers that precipitate during polymerization, such as methacrylic acid, dissolution, and swelling capacity, the polymer is reduced. Similar effects could be achieved by proper starting viscosity. Too high viscosity has to be avoided to ensure unhindered flow of the uncured resin beneath the last built layer. Suitable thickeners are fillers based on water-soluble polymers such as PVP.

Crosslinking agents based on bifunctional monomers give a fast increase in formulation viscosity during irradiation. Reduced swelling and limited radical diffusion give significantly increased resolution and mechanical properties. The solubility of the polymer can be maintained by using hydrolytically cleavable crosslinking agents such as methacrylic anhydride.

RP with optimized formulations showed that it is possible to shape sacrificial, water-soluble structures by using stereolithography and commercially available monomers. By tuning the composition of the photopolymerizable formulation, solubility, feature resolution, and mechanical properties can be adjusted to the requirements of the application. The photopolymers developed for this work were shown to be suitable for the fabrication of sacrificial cellular structures with feature resolutions around 200 μm. Parts made by this process can be dissolved in about 2 h in 1*N* NaOH at 50°C. Such sacrificial structures will help to solve current problems in molding of advanced materials.

We acknowledge the financial support of the Hochschuljubiläumsstiftung of the City of Vienna and support by the Austrian Science Foundation FWF under contract P15859.

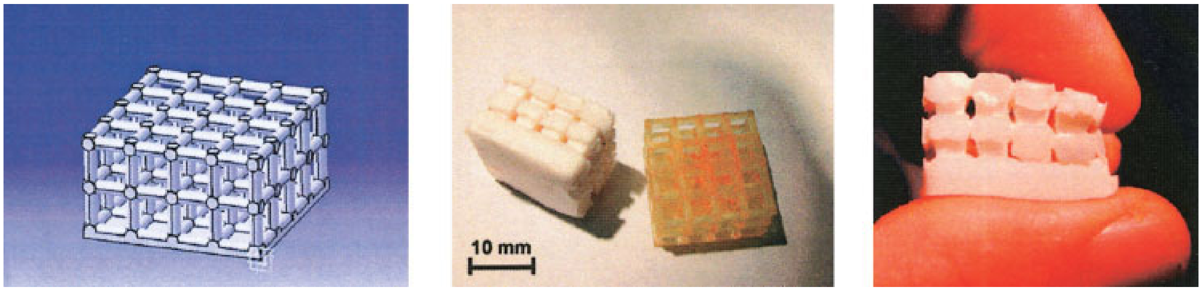


Figure 18 Cellular test structure (left) made of water-soluble photopolymers (middle) and molded silicone structure (right).

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